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Yue, Yuanzheng; Qiao, A.; Bennett, T.D.; Zhang, J.Y.; Tao, H.Z.

Published in:
The 24th International Congress on Glass - Abstracts

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Unspecified

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

[Link to publication from Aalborg University](#)

Citation for published version (APA):
Yue, Y., Qiao, A., Bennett, T. D., Zhang, J. Y., & Tao, H. Z. (2016). Melting Behaviour of Zeolitic Imidazolate Frameworks. In *The 24th International Congress on Glass - Abstracts* (pp. 112). International Commission on Glass (ICG).

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Melting Behaviour of Zeolitic Imidazolate Frameworks

Y.Z. Yue^{1,2}, A. Qiao¹, T.D. Bennett,³ J.Y. Zhang¹, H.Z. Tao¹

¹State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China.

²Department of Chemistry and Bioscience, Aalborg University, DK-9220 Aalborg, Denmark.

³Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, United Kingdom

yy@bio.aau.dk

It has been reported that certain members of the zeolitic imidazolate framework (ZIF) family can be melted and vitrified under optimal synthetic and thermal conditions.¹ For instance, ZIF-4 [$\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$] has been proven to be a good glass former. Upon heating in inert gas, the synthesized ZIF-4 undergoes a series of abrupt enthalpy changes due to the following events. The remaining solvents are first removed, causing the long range order structure to collapse to a low-density amorphous (LDA) phase. The LDA phase is then rapidly transformed into a high-density amorphous (HDA) phase, subsequently into a viscous high-density liquid (HDL) phase, and then crystallizes into the densest member of the ZIF family, i.e., ZIF-zni. Upon further heating, ZIF-zni is melted, and its liquid survives for about 10 degrees above the liquidus temperature, and is finally decomposed into various chemical species and gases, leading to formation of foam glass. If the melt is quenched at a rate of >20 K/min prior to decomposition, bulk glass is obtained. However, recent investigations into other ZIFs have shown that their enthalpic responses to dynamic heating greatly differ from that of ZIF-4.

Here, as an example we study the melting and vitrifying behaviors of ZIF-62 ($\text{Zn}(\text{Im})_{1.75}(\text{bIm})_{0.25}$), and illustrate some striking difference in phase transitions between ZIF-62 and ZIF-4. As shown in Figure 1, upon the differential scanning calorimeter (DSC) upscanning, the sample first undergoes a desolvation-induced endothermic response over a temperature range of 200 K, and then a weak amorphization-induced exothermic response, and finally a melting event above 675 K. When the fresh sample is pre-treated at 443 K in vacuum and subsequently is upscanned in DSC, the desolvation peak almost disappears, but the amorphization and the melting peaks are still present. This implies that most of solvent has already been released during pre-heat treatment. Since no crystallization peak appears during the DSC upscanning, the long-range structural order of ZIF-62 must survive to large extent upon solvent release, i.e., only a small fraction of structurally ordered domains collapse to the amorphous state. This implies that the melting peak of ZIF-62 is due to the melting of the original crystal structure of ZIF-62. This is evidently in contrast to ZIF-4, the melting peak of which has been attributed to melting of the ZIF-zni crystals.

Furthermore, pre-heat treatment below the glass transition temperature (T_g) for certain duration has a strong impact on the melting behavior of ZIF-62, which is manifested as the gradual shift of the melting peak to lower temperatures with increasing the pre-heat treatment temperatures (Figure 1). The 443 K treated ZIF-6 sample is subjected to two DSC upscans as shown in Figure 2. It is seen that after the melting (upscan 1) and subsequent cooling processes, the melt has been transformed to bulk glass. This is verified by the occurrence of the glass transition peak during DSC upscan 2. This result means that ZIF-62 is a good glass former. Its T_g value is determined to be 596 K.

Key issues discussed here include factors governing the melting of ZIFs, and the origin of the shift of the melting peak upon pre-heat treatment.

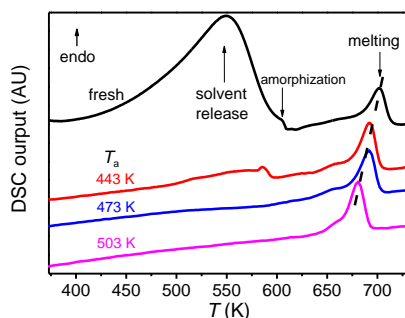


Figure 1. The DSC upscans of both the fresh ZIF-62 sample and the samples pre-heat treated at different temperatures (T_a) for 18 hours in vacuum. The upscan was conducted at 10 K/min in argon. AU: arbitrary unit.

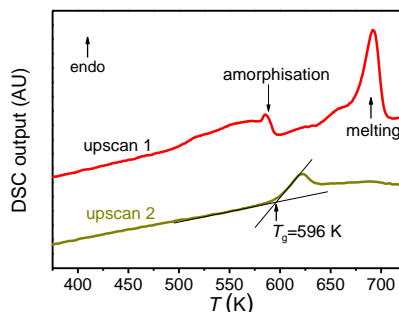


Figure 2. The DSC upscans of ZIF-62. The as-synthesized sample was first pre-heat treated at 443 K for 18 hours in vacuum, and then subjected to DSC upscans 1 and 2. The upscan was conducted at 10 K/min in argon.

1) T. D. Bennett, J. C. Tan, Y. Z. Yue, E. Baxter, C. Ducati, N. J. Terrill, H. H. M. Yeung, Z. Zhou, W. Chen, S. Henke, A. K. Cheetham, G. N. Greaves, Hybrid Glasses from Strong and Fragile Metal-Organic Framework Liquids, *Nature Commun.* **6** (2015) 8079.